Use of Symmetric Rank-One Hessian Update in Molecular Geometry Optimization

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ABSTRACT: The use of the symmetric rank-one Hessian update and the Broyden–Fletcher–Goldfarb–Shano (BFGS) update formula are considered in an *ab initio* molecular geometry optimization algorithm. It is noted that the symmetric rank-one Hessian update has an advantage when compared with the BFGS update formula and this advantage must be more evident in the optimization of molecular geometry, because the total energy surface is a near-quadratic function with a small nonlinearity close to a minimum point. The results obtained in geometry optimization of a test group of molecules support this proposal and show that the use of the symmetric rank-one Hessian update formula permits reduction of the number of energy and gradient evaluations needed to locate a minimum on the energy surface. J Comput Chem 19: 1877–1886, 1998

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Introduction

The knowledge of the geometrical structure of molecules is very important in many areas of chemistry. *Ab initio* quantum-mechanical calculations have recently become an efficient way to determine the geometry of polyatomic molecules. This progress, in general, has been reached due to the introduction of the analytical derivative method[1–5] in the quasi-Newton optimization technique.[6,7] Later, some modifications of the quasi-Newton method employing analytical derivatives were proposed.[8–12] In all of these methods only the first-order derivatives are needed for optimization of molecular geometry. Presently, the analytical expressions of first-order derivatives are known

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for most types of wave functions[2–5] and are widely used in molecular geometry optimization.

It is well known that the convergence of quasi-Newton optimization methods depends mainly on the formula applied for updating the Hessian matrix, the algorithm controlling the step size, and the coordinate system used in the calculation.[6,7] In this study, the influence of updating the Hessian formula on the convergence of a quasi-Newton minimization method is investigated. The Davidon–Fletcher–Powell (DFP) formula,[13–15] the symmetric rank-one (SR1) formula,[16] and the Broyden–Fletcher–Goldfarb–Shano (BFGS)[17–20] formula are most widely used in minimization algorithms and, in particular, in molecular geometry optimization.[21,22] The first numerical experience using these formulas in minimization algorithms has shown that the BFGS update is the best.[6]

Interest in obtaining the best update formula, however, has now been renewed. Results of recent numerical experiments have shown that a minimization method using the SR1 update formula may be competitive numerically with that based on the BFGS formula.[23–28] A theoretical comparison of a minimization algorithm using the SR1 update and that using the BFGS update does not show obvious advantages for the SR1 formula for nonquadratic functions.[23–28] Nevertheless, for positive definite quadratic functions there is a theorem which states that the optimization procedure with the SR1 update formula and a line-search method reaches the solution in, at most, n + 1 iterations and, if n + 1 iterations are required, then the final Hessian approximation is the actual Hessian at the solution.[29] This theorem is not generally true for the BFGS update unless an exact line search is used. In other words, this theorem points to some of the advantages of using the SR1 update formula as compared with the BFGS update for quadratic functions.

For molecules we know that the anharmonic force constants are much smaller than the harmonic force constants. This means that, near an equilibrium point, the energy surface of a molecule is nearly a quadratic function with only a slight nonlinearity. We can therefore suppose that the use of the SR1 update formula in a molecular geometry optimization procedure may be more successful than the use of the BFGS formula.

To test this proposal, a geometry optimization algorithm has been developed and employed in the MOLPACK program for *ab initio* calculation of atoms and molecules. The results of the present investigation of update formulas are presented in the following order: A brief description of the optimization algorithm used in this work is given in the next section. The convergence criterion used for termination of the optimization procedure is described in the third section. Finally, a comparative analysis of the results obtained under geometry optimization of test molecules with the SR1 and BFGS update formulas and conclusions are presented.

Molecular Geometry Optimization Algorithm

The general structure of the optimization algorithm used in the present investigation is as follows:

Step 1. Evaluate the Hartree–Fock total energy and gradient, g_0, of a molecule at the initial point. Set initial Hessian, H_0.

Step 2. Calculate the Euclidean norm of the gradient vector and check the convergence criterion.

Step 3. Compute a quasi-Newton direction s_k.

3.1. Check positive definiteness of the Hessian, H_k, and solve:

$$\left(H_k + \sum_i \lambda_{ki} P_{ki}\right) s_k = -g_k \qquad (1)$$

3.2. If the Euclidian norm of s_k is greater than 0.5 a.u., then renormalize s_k to 0.5 a.u.

Step 4. Find an acceptable step length, α_k, by use of a line-search method.

4.1. Set $\alpha_k = 1.0$.

4.2. If $E(x_{k+1}) \leq E(x_k) + \lambda \alpha_k g_k^T s_k$, where $\lambda = 0.0001$, then go to step 5.

4.3. Otherwise, select new α_k such that $x_{k+1}(\lambda)$ is the local minimizer of the one-dimensional quadratic interpolating $E(x_k)$, $g_k^T s_k$, and $E(x_{k+1})$, but constrain the new α_k to be ≥ 0.1, or else select the new α_k such that $x_{k+1}(\alpha)$ is the local minimizer of the one-dimensional cubic interpolating $E(x_k)$, $g_k^T s_k$, $E(x_{k+1}(\alpha_{\text{prev}}))$, and $E(x_{k+1}(\alpha_{2\text{prev}}))$, but containing the new α_k to be in $[0.1\alpha_{\text{prev}}, 0.5\alpha_{\text{prev}}]$. Here, $x_{k+1}(\alpha) = x_k + \alpha s_k$ and α_{prev} and $\alpha_{2\text{prev}}$ are previous two step lengths.

4.4. Go to step 4.2.

Step 5. Calculate new molecular geometry:

$$x_{k+1} = x_k + \alpha_k s_k$$

Step 6. Evaluate the Hartree–Fock total energy and gradient g_k of a molecule at the current geometry.

Step 7. Update the Hessian matrix by using the (a) SR1 update formula:

$$H_{k+1} = H_k + \frac{(y_k - H_k \delta_k)(y_k - H_k \delta_k)^T}{\delta_k^T (y_k - H_k \delta_k)} \quad (2)$$

and the (b) BFGS update formula:

$$H_{k+1} = H_k + \frac{y_k y_k^T}{y_k^T \delta_k} - \frac{H_k \delta_k \delta_k^T H_k}{\delta_k^T H_k \delta_k} \quad (3)$$

where:

$$y_k = g_{k+1} - g_k, \quad \delta_k = x_{k+1} - x_k.$$

Step 8. Put $k = k + 1$, and go to step 2.

It is well known that the BFGS update formula preserves the positive definiteness of the Hessian matrix if the original Hessian is positively defined.[6] For other updates this is not valid. Therefore, to keep the positive definiteness of the Hessian matrix, the modified Newton equation [eq. (1)] is used in the present algorithm. This equation is similar to that used in the Levenberg–Marquardt[30,31] and rational function[9,10] optimization method:

$$(H_k + \nu I) s_k = -g_k$$

The difference between them is that, in eq. (1), the local mode approximation has been used. Optimal value of the ν parameter can be defined by different methods.[6] In the present investigation, we used an approach based on direct controlling of the positive definiteness of the Hessian matrix. The positive definiteness can be controlled by calculating eigenvalues and eigenvectors of the Hessian matrix at each iterative step k. For all positive eigenvalues less then $1.0 * 10^{-5}$ the values of the corresponding parameters, λ_{ki}, are chosen to set the eigenvalues of the modified Hessian matrix equal to $1.0 * 10^{-5}$, whereas λ_{ki} values are set to zero for all other positive eigenvalues. For each negative eigenvalue, the Hessian matrix is modified by adding to it a positively defined matrix $\lambda_{ki} P_{ki}$, where P_{ki} is projector on an appropriate eigenspace. The real constant λ_{ki} is chosen to set a negative eigenvalue of modified Hessian matrix equal to 0.1 a.u. if the initial eigenvalue was greater than -0.1; otherwise, it is chosen to equal 0.4 a.u. Projector P_{ki} is calculated from the corresponding eigenvector of the Hessian matrix.

Restriction of the minimal eigenvalues of the Hessian matrix results in a restriction of the s_k step length. When the Hessian has small eigenvalues, the step length may be longer than the optimal one. Therefore, a restriction of the step length is often used in optimization methods.[6] Restriction of smallest eigenvalues of the Hessian is similar to introducing the maximal allowed length of each step length component. The total step length is also restricted in the algorithm. At step 3.2 the s_k step length is renormalized to 0.5 a.u. if the Euclidian norm of s_k exceeds 0.5 a.u.

In a recent investigation[28] it was shown that the use of an updating formula at each optimization step is more effective than to skip some of them at the rejected steps. Therefore, this strategy was employed in the algorithm just described. The update formulas (2) and (3) have been programmed directly without modifications.

The convergence of the minimization method just given depends on the successful determination of the optimal step length α_k at step 4. There are different approaches to determining an optimal step length in minimization algorithms.[6] In the present method, the inexact line search algorithm A6.3.1, described in ref. 32, has been employed. This algorithm differs from an exact line-search method in that an exact line search is applied in this algorithm if condition 4.2 is not fulfilled. Note that the exact line-search algorithm is used often in quantum chemical programs for optimization of molecular structures.[8]

Convergence Criteria

Two stopping criteria are commonly used in molecular geometry optimization.[33,34] The first criterion[33] is stronger. According to this criterion the optimization process is terminated if the maximum gradient component is less than 0.0003 a.u. and either the total energy change from the previous cycle is less than 10^{-6} hartree or the maximum predicted displacement is less than 0.0003 a.u. per coordinate. This criterion has been introduced to handle both rigid and flexible molecules.

The present investigation has shown that this criterion is too strong to treat large molecules. This can be understood by considering possible changes of atomic coordinates under molecular geometry optimization. These possible changes of coordinates include those in which:

1. Small changes in coordinates of atoms cause a small change in the molecular total energy.
2. Small changes in coordinates of atoms cause a strong change in the molecular total energy.
3. Large changes in coordinates of atoms cause a small change in the molecular total energy.

Changes of type 1 correspond to a point on a total energy hypersurface that is relatively distant from critical points. Near to critical points the coordinate changes of types 2 and 3 are most important. In particular, near a minimum point, the total energy hypersurface can be approximated by a quadratic function. Therefore, typical changes of atomic coordinates in the vicinity of a minimum point are of type 2. Changes of coordinates near a saddle point are very important under molecular geometry optimization, because they describe rearrangement of atoms near a transition state and a rotation of a group of atoms with respect to other atoms. Such changes lead to a significant modification of molecular structure without a large change in total molecular energy. Hence, near a saddle point, typical changes of some atomic coordinates are of the type 3, whereas, for the remaining coordinates, they are of types 1 or 2.

Thus, we can see that the stopping criterion of an optimization algorithm, which includes termination of an optimization procedure if the total energy change between successful optimization steps is less than a defined threshold, or termination if the maximum predicted displacement is less than a defined value, can terminate an optimization procedure before a minimum point can be reached.

Therefore, in the present investigation, the stopping criterion employed has included only one criterion: The optimization process is terminated when the maximal Euclidean norm of the gradient vector is less than 0.0001 a.u. This convergence criterion is more strict compared with that described in ref. 33, and it leads to a greater number of optimization cycles. However, the increase of optimization step number is justified by a more reliable determination of molecular structures.

Results and Discussion

The appropriate choice of trial molecules is very important for proper testing of a minimization algorithm. It is well known that the minimization methods are derived by considering that an initial function can be approximated near a minimum point by a function without critical points. Therefore, molecular total energy surfaces used in testing minimization algorithms should not have intermediate local minima or saddle points between initial and minimum points. Such points can significantly change convergence of a minimization method and the correct answer may not be obtained in test calculations. Unfortunately, complete molecular potential energy surfaces are, as a rule, unknown for polyatomic molecules. Therefore we cannot select test molecules with absolute confidence. However, we can choose only the molecules that do not have critical points between initial and minimum points.

A test group of 30 molecules has been proposed recently in ref. 33. It is used often in investigations of minimization algorithms.[33–36] Optimization of geometries of these test molecules carried out in the present work has shown that minimum points of seven of them are lower than those reported in ref. 33. For the methylamine, ACANIL01, benzidine, pretin, mesityloxide, and caffeine molecules, optimization algorithms have converged to the minimum points directly from the starting geometries presented in ref. 33. Optimized geometries of these molecules, together with total energies obtained using the STO-3G basis[37] are presented in Appendix Table AI. Comparison of the total energies and equilibrium geometries with corresponding ones from ref. 33 show that the newly determined minima are relatively distant from the starting points, and the differences in the equilibrium geometries result, in most cases, from rotations of groups of atoms with respect to the others.

For the 2-hydroxybi-cyclopentane molecule, the minimization procedure has converged to the minimum point determined in ref. 33. However, the character of convergence suggests that, between initial and final points, there is probably a critical point, and hence another conformer might have total energy that is close to the known one. In this connection, the starting geometry for this molecule has been changed in accordance with general ideas of structural chemistry. With this starting point a new minimum point has been located with a lower

TABLE I.
Hartree – Fock Total Energies[a] (with Reversed Sign) of Test Molecules at Their Minimum Points.

Molecule	Basis	E_{tot}
Water	STO-3G	74.965901
	3-21SP	75.768788
	4-22SP	75.931913
	(9s5p / 5s3p)	76.019243
Ammonia	STO-3G	55.455420
	3-21SP	56.003404
	4-22SP	56.111287
	(9s5p / 5s3p)	56.186373
Ethane	STO-3G	78.306180
	3-21SP	79.012433
	4-22SP	79.098881
	(9s5p / 5s3p)	79.212430
Acetylene	STO-3G	75.856248
	3-21SP	76.577386
	4-22SP	76.685664
	(9s5p / 5s3p)	76.813862
Allene	STO-3G	114.421719
	3-21SP	115.485272
	4-22SP	115.647558
	(9s5p / 5s3p)	115.845490
Hydroxysulphane	STO-3G	468.125914
	3-21SP	472.728498
	4-22SP	473.144014
Benzene	STO-3G	227.891361
	3-21SP	229.968221
	4-22SP	230.309998
	(9s5p / 5s3p)	230.663613
Ethanol	STO-3G	152.132674
	3-21SP	153.614974
	4-22SP	153.855069
	(9s5p / 5s3p)	154.059294
Acetone	STO-3G	189.536032
	3-21SP	191.343039
	4-22SP	191.645939
	(9s5p / 5s3p)	191.923054
Disilylether	STO-3G	648.580023
	3-21SP	655.278189
	4-22SP	655.670071
1,3,5-Trisilacyclohexane	STO-3G	976.132408
	3-21SP	986.044289
	4-22SP	986.576383
Benzaldehyde	STO-3G	339.120842
	3-21SP	342.294267
	4-22SP	342.854983
1,3-Difluorobenzene	STO-3G	422.811055
	3-21SP	427.020248
	4-22SP	427.824496
1,3,5,-Trifluorobenzene	STO-3G	520.270521
	3-21SP	525.540849
	4-22SP	526.577534
Neopentane	STO-3G	194.046770
	3-21SP	195.790786
	4-22SP	196.036069
Furan	STO-3G	225.751256
	3-21SP	227.899789
	4-22SP	228.258705
Napthalene	STO-3G	378.686850
	3-21SP	382.119494
	4-22SP	382.713976
1,5-Difluoronapthalene	STO-3G	573.606333
	3-21SP	579.175621
	4-22SP	580.229221
ACHTAR10	STO-3G	356.282645
	3-21SP	359.739138
	4-22SP	360.321999
Difuropyrazine	STO-3G	556.719104
	3-21SP	561.955275
Histidine	STO-3G	538.549102
	3-21SP	543.744452
Dimethylpentane	STO-3G	271.200877
	3-21SP	273.639417
Mentone	STO-3G	458.446388

[a]Total energies in E_h.

total energy than that previously reported. The initial and new minimum points of this molecule as well the corresponding total energies calculated with STO-3G basis sets are presented in Appendix Table AII. For these reasons, the seven molecules just mentioned have been excluded from the test group of molecules proposed in ref. 33. The other 23 molecules have been used in the investigation of the update formulas presented in this work.

This investigation of the test group of molecules permits us to note the suggestion in ref. 33 that optimizations in natural internal coordinates show a strong tendency to converge to global minima, whereas Cartesian optimizations tend to converge to the local minimum closest to the starting geometry, is very important in practice for molecular geometry optimizations. However, the present calculations indicate that this proposal is not so obvious and it should be investigated more carefully.

It is well known that the properties of update formulas do not depend on the coordinate system used. However, the convergence of an optimization method depends on the coordinate system employed as well the initial Hessian. Therefore, geometries of test molecules have been optimized in the Cartesian and in the internal coordinate system with different initial Hessians to demonstrate that the main conclusion of the present in-

TABLE II.
Comparison of Total Number of Function and Gradient Evaluations for an Optimization Procedure with SR1 and BFGS Updates.

		Cartesian				Internal							
		Unit				Unit				Diagonal[a]			
		BFGS		SR1		BFGS		SR1		BFGS		SR1	
Molecule	Basis	Func.	Grad.	Func.	Grad.	Func.	Grad.	Func.	Grad.	Func.	Grad.	Func.	Grad.
Water	STO-3G	5	5	6	6	9	9	7	7	6	6	6	6
	3-21SP	7	7	5	5	9	9	7	7	5	5	6	6
	4-22SP	7	7	5	5	8	8	5	5	6	6	4	4
	(9s5p / 5s3p)	7	7	5	5	8	8	5	5	5	5	4	4
Ammonia	STO-3G	7	7	7	6	9	9	7	7	6	6	6	6
	3-21SP	8	8	5	5	9	9	6	6	7	7	5	5
	4-22SP	8	8	6	6	9	9	6	6	5	5	5	5
	(9s5p / 5s3p)	8	8	7	7	8	8	7	7	7	7	8	7
Ethane	STO-3G	7	7	6	6	8	8	7	7	5	5	5	5
	3-21SP	10	10	6	6	9	9	6	6	6	6	5	5
	4-22SP	10	10	7	7	10	10	7	7	6	6	5	5
	(9s5p / 5s3p)	9	9	7	7	9	9	7	7	6	6	5	5
Acetylene	STO-3G	7	6	6	5	5	5	5	5	5	5	5	5
	3-21SP	6	5	7	6	5	5	5	5	4	4	4	4
	4-22SP	5	5	7	7	5	5	6	6	5	5	4	4
	(9s5p / 5s3p)	6	5	7	6	5	5	5	5	4	4	4	4
Allene	STO-3G	10	10	7	7	9	9	8	7	6	6	6	6
	3-21SP	9	9	7	7	10	10	7	7	7	7	5	5
	4-22SP	9	9	6	6	10	10	7	7	7	7	5	5
	(9s5p / 5s3p)	10	10	6	6	9	9	7	7	7	7	5	5
Hydroxysulphane	STO-3G	22	22	19	17	25	25	20	20	16	16	14	13
	3-21SP	24	24	21	20	27	27	24	23	18	18	17	16
	4-22SP	25	25	23	22	27	27	23	20	19	19	16	15
Benzene	STO-3G	7	7	4	4	5	5	5	5	4	4	4	4
	3-21SP	7	7	6	6	5	5	5	5	4	4	6	5
	4-22SP	6	6	5	5	7	7	6	6	4	4	4	4
	(9s5p / 5s3p)	6	6	5	5	5	5	5	5	3	3	4	4
Ethanol	STO-3G	24	24	19	17	20	20	14	14	12	12	11	11
	3-21SP	27	27	21	20	38	38	26	23	14	14	11	11
	4-22SP	27	27	19	18	24	24	15	15	14	14	11	10
	(9s5p / 5s3p)	25	25	18	17	22	22	16	15	11	11	11	11
Acetone	STO-3G	23	23	15	14	16	16	14	13	14	14	13	12
	3-21SP	24	24	14	13	24	24	15	15	16	16	14	13
	4-22SP	25	25	16	15	22	22	14	14	15	15	12	12
	(9s5p / 5s3p)	23	23	15	14	20	20	13	13	12	12	10	10

TABLE II.
(Continued)

		Cartesian				Internal							
		Unit				Unit				Diagonal[a]			
		BFGS		SR1		BFGS		SR1		BFGS		SR1	
Molecule	Basis	Func.	Grad.	Func.	Grad.	Func.	Grad.	Func.	Grad.	Func.	Grad.	Func.	Grad.
Disilylether	STO-3G	27	27	21	20	22	22	20	19	18	18	17	16
	3-21SP	35	35	26	25	31	31	22	20	25	25	23	21
	4-22SP	37	37	28	28	33	32	24	23	25	25	21	20
1,3,5-Trisilacyclohexane	STO-3G	37	37	22	21	34	34	30	27	17	17	19	16
	3-21SP	43	43	22	22	39	39	33	30	20	20	16	16
	4-22SP	37	37	25	24	39	39	27	26	19	19	16	15
Benzaldehyde	STO-3G	31	31	28	24	18	18	14	14	10	10	11	10
	3-21SP	36	36	32	27	22	22	16	15	13	13	12	11
	4-22SP	35	35	25	24	21	21	17	16	13	13	11	10
1,3-Difluorobenzene	STO-3G	15	15	13	12	16	16	12	12	10	10	9	9
	3-21SP	21	21	16	15	21	21	16	15	13	13	11	11
	4-22SP	21	21	15	15	23	23	16	16	13	13	11	10
1,3,5,-Trifluorobenzene	STO-3G	10	10	8	8	17	17	12	12	10	10	8	8
	3-21SP	9	9	9	9	20	20	14	14	14	14	11	10
	4-22SP	10	10	9	8	21	21	14	13	14	14	11	11
Neopentane	STO-3G	11	11	7	7	8	8	7	7	6	6	6	6
	3-21SP	12	12	7	7	11	11	7	7	6	6	6	5
	4-22SP	12	12	7	7	9	9	7	7	6	6	4	4
Furan	STO-3G	12	12	10	10	16	16	15	14	10	9	10	10
	3-21SP	19	19	13	12	18	18	12	11	11	10	11	10
	4-21SP	19	19	15	13	14	14	12	11	11	10	8	8
Napthalene	STO-3G	17	17	12	12	38	29	35	27	48	28	37	24
	3-21SP	17	17	12	12	42	35	39	30	48	27	43	28
	4-22SP	16	16	13	13	42	34	39	29	48	27	41	26
1,5-Difluoronapthalene	STO-3G	19	19	19	17	19	19	15	14	12	12	11	11
	3-21SP	23	23	19	18	24	24	19	18	14	14	14	13
	4-22SP	23	23	19	18	24	24	17	17	13	13	13	12
ACHTAR10	STO-3G	102	102	68	62	51	51	36	33	15	15	17	16
	3-21SP	131	130	85	78	66	66	48	43	27	26	27	24
	4-22SP	109	109	64	58	68	67	42	40	22	22	20	18
Difuropyrazine	STO-3G	24	24	22	19	46	37	47	34	60	33	51	34
	3-21SP	27	27	22	21	44	37	40	32	56	32	49	33
Histidine	STO-3G	143	140	124	105	89	85	82	73	35	33	42	37
	3-21SP	206	196	157	139	107	107	117	100	41	38	47	44
Dimethylpentane	STO-3G	165	158	100	87	55	55	38	37	20	20	20	17
	3-21Sp	145	144	90	85	78	76	43	41	21	21	20	19
Mentone	STO-3G	106	106	102	90	57	56	45	42	18	17	19	19

[a]Ref. 38.

vestigation does not depend on the type of coordinate system and initial Hessian chosen.

The unit matrix has been used as the initial Hessian with both coordinate systems. In addition, the initial diagonal Hessian proposed in ref. 38, with the restriction that its minimal value is equal to 0.05, has been used with the internal coordinate system. Geometries of all selected molecules have been optimized using the STO-3G basis set. Also, geometries of smaller molecules have been optimized in the 3-21SP,[39] 4-22SP,[39] and (9s5p/5s3p)[40] basis sets. The restricted Hartree–Fock method has been employed in all these calculations.

The Hartree–Fock total energies of test molecules that correspond to the minimum points are presented in Table I. These total energies have been repeated in all calculations. The total energies of the molecules calculated with the STO-3G basis sets are equal to those obtained in ref. 33. The number of energy and gradient evaluations needed to reach the energy minimum with the SR1 and BFGS update formulas are presented in Table II. These represent the main results of the present investigation.

Analysis of the data presented in Table II shows that, on average, for all test calculations, the optimization procedure with the BFGS update required 25.8% and 33.2% more energy and gradient evaluations, respectively, than with the SR1 update formula. Individually, results indicate that: (1) the BFGS update required 35.5% and 45.8% more evaluations for the Cartesian coordinates; (2) for an internal coordinate system with the unit initial Hessian, the BFGS update required 26.2% and 34.1% more evaluations; and (3) with the diagonal initial Hessian, 9.2% and 10.0% more energy and gradient evaluations were required in comparison to the SR1 update formula.

The results obtained show that the SR1 update is more effective in Cartesian coordinates than in internal ones. To understand this, it must be noted that a comparison of internal and Cartesian coordinates indicates that the difference between the various components of internal coordinates (e.g., between stretch and angular coordinates) is much larger than that between components of the Cartesian coordinates. This means that the Cartesian coordinates are more homogeneous as compared with internal ones, and thus a molecular potential energy surface in internal coordinates is more nonlinear than in Cartesian coordinates. Therefore, according to the main suggestion of the present investigation, given in the Introduction, a minimization algorithm with an SR1 update must be relatively more effective as compared with a BFGS update in Cartesian coordinates than in the internal ones. Results of the test calculations are in direct accordance with this conclusion.

Thus, the results of the present investigation show that the use of the SR1 update formula allows for a reduction in the number of energy and gradient evaluations in a minimization method needed to reach a minimum point on the molecular total energy surface.

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Appendix

TABLE AI.
Optimized Geometries and Corresponding Total Energies of Molecules (Cartesian Coordinates in Å, Total Energies in a.u.).

	Methylamine (E_{tot} − 94.032863)		
	X	Y	Z
H1	−0.842525177	−1.275152338	−0.124048595
N2	0.097707593	−0.883606624	−0.298633287
C3	0.023359843	0.577596035	−0.041201272
H4	1.014333863	1.012067624	−0.162031579
H5	0.689467962	−1.296721572	0.440969185
H6	−0.341693550	0.830285806	0.957703436
H7	−0.640350552	1.035531008	−0.772757887
	ACANIL01 (E_{tot} − 432.033485)		
	X	Y	Z
C1	−2.129550196	−1.337177450	0.455715165
C2	−0.794113387	−1.526845136	0.142530958
C3	−0.044121110	−0.489030157	−0.409609060
C4	−0.662069832	0.736347101	−0.657309892
C5	−1.994279159	0.922785663	−0.329049677
C6	−2.732778513	−0.110096145	0.228676071
N7	1.338159045	−0.716625338	−0.786222191
C8	2.449473165	−0.117228626	−0.074591214
C9	2.254277085	1.309027353	0.471507050
O10	3.498994724	−0.730880993	0.015472579
H11	−2.700238304	−2.152108016	0.883338632
H12	−0.325079858	−2.485927146	0.320462792
H13	−0.099702485	1.537132664	−1.115634464

TABLE AI.
(Continued)

H14	−2.462552808	1.879895756	−0.522154591
H15	−3.775203120	0.038725771	0.477576466
H16	1.530995312	−1.717508166	−0.910472598
H17	3.149408406	1.595336326	1.013757327
H18	1.400927061	1.356359682	1.140448476
H19	2.097453973	2.007816856	−0.344441829

Benzidine (E_{tot} − 563.291440)

	X	Y	Z
C1	−1.119949789	0.455445025	2.844942235
C2	−1.114841366	0.416369441	1.463499952
C3	0.017756235	0.020683057	0.751771540
C4	1.150338933	−0.337321425	1.483349257
C5	1.155099496	−0.304547122	2.864916007
C6	0.016818730	0.091897467	3.564244632
C7	0.017762096	−0.020686093	−0.751771369
C8	−1.114869428	−0.416253354	−1.463511926
C9	−1.119967384	−0.455327758	−2.844954338
C10	0.016846819	−0.091899079	−3.564244522
C11	1.155161765	0.304425777	−2.864903608
C12	1.150390070	0.337200088	−1.483336932
N13	0.040469258	0.200886940	5.004032217
N14	0.040501825	−0.200889627	−5.004031933
H15	−2.007990558	0.770546207	3.376018027
H16	−2.007983330	0.710706086	0.927690222
H17	2.042671811	−0.661512458	0.963622695
H18	2.042800223	−0.592440336	3.411788481
H19	−2.008047966	−0.710496486	−0.927711819
H20	−2.008035784	−0.770335265	−3.376039505
H21	2.042898294	0.592226280	−3.411766760
H22	2.042751289	0.661297703	−0.963600785
H23	0.680227337	−0.497316427	5.405738568
H24	−0.895598591	0.024348051	5.392328341
H25	−0.895544090	−0.024256832	−5.392338167
H26	0.680334130	0.497250138	−5.405730640

Pretin (E_{tot} − 569.853832)

	X	Y	Z
C1	−0.691616574	−0.708315895	−0.002871376
C2	−0.485199247	0.675539106	−0.027374701
N3	−1.930835861	−1.278460513	0.027348935
N4	−1.539012579	1.557726274	−0.016253519
C5	−2.947352051	−0.406295450	0.038474657
C6	−2.747536353	0.983271438	0.017201774
C7	0.486297285	−1.650634688	−0.023957080
N8	1.729629717	−0.934791361	−0.010130604
C9	1.806895733	0.462131808	−0.071974146
N10	0.806823059	1.291481170	−0.061285580
O11	0.453375194	−2.868296703	−0.044984211
N12	3.138790195	0.972017523	−0.203201739
H13	−3.952834211	−0.814109180	0.064416063

TABLE AI.
(Continued)

H14	−3.605976470	1.650419391	0.027409209
H15	2.588645403	−1.472204685	−0.135146149
H16	3.117657067	1.990543671	−0.067476217
H17	3.772249696	0.549978097	0.489804683

Mesityloxide (E_{tot} − 304.063144)

	X	Y	Z
C1	−1.605985564	−1.192182508	−0.134935015
C2	−0.947907574	0.175933976	0.016416747
C3	−1.929028797	1.341102880	0.140765639
C4	0.357080940	0.383489895	0.042938103
C5	1.452663642	−0.656483552	−0.067206115
C6	2.885419881	−0.081644739	−0.000353261
O7	1.259059279	−1.857443706	−0.198926533
H8	−0.860800914	−1.973611623	−0.217634837
H9	−2.241621191	−1.394326518	0.723834575
H10	−2.235406610	−1.204211888	−1.021543315
H11	−2.567257298	1.392089160	−0.738617371
H12	−1.407588653	2.286510594	0.245714155
H13	−2.572800110	1.201406085	1.006400991
H14	0.722981784	1.395034415	0.154606469
H15	3.036548095	0.437909958	0.941738118
H16	3.041576066	0.628396748	−0.807726855
H17	3.613066994	−0.881969066	−0.085471494

Caffeine (E_{tot} − 667.735916)

	X	Y	Z
C1	0.799456606	−0.262457687	−0.007050142
C2	−0.278297341	−1.083922949	−0.015385836
N3	1.918702491	−1.107822034	−0.035654500
N4	0.083868884	−2.436571608	−0.048315185
N5	−1.599340562	−0.600435072	0.007092737
C6	1.411481888	−2.387349955	−0.059166436
C7	0.713672119	1.213048075	0.026091223
C8	−1.833100298	0.807580760	0.040084243
N9	−0.661431318	1.641769774	0.047856246
O10	1.639451361	2.011948090	0.035297147
O11	−2.955070231	1.288466982	0.060717014
C12	−0.926906773	3.091089534	0.082037374
C13	−2.744002178	−1.522471787	−0.002843590
C14	3.335956639	−0.704968334	−0.039553052
H15	2.065735392	−3.252262421	−0.084021176
H16	−1.501752856	3.401777539	−0.791350842
H17	−1.485849798	3.362952328	0.978394053
H18	0.032706208	3.603349917	0.084652268
H19	−2.736096533	−2.138810796	−0.903208732
H20	−3.651452638	−0.921591747	0.018484217
H21	−2.720174724	−2.177680781	0.869353219
H22	3.951428637	−1.602730870	−0.064786661
H23	3.568484338	−0.130927610	0.858857924
H24	3.552530787	−0.091979706	−0.915951713

TABLE AII.
Initial and Optimized Geometries and Corresponding Total Energies of 2-Hydroxybicyclopentane Molecule (Cartesian Coordinates in Å, Total Energies in a.u.).

	Initial geometry (E_{tot} − 253.194096)		
	X	Y	Z
C1	−0.931351100	0.214977849	0.190692562
C2	0.315392341	0.598474431	0.989406722
H3	−0.177471961	−1.000187287	−1.000098050
C4	1.072721805	−0.575403758	0.391514438
H5	−1.807798062	−0.161028814	0.754214900
C6	−0.867416297	−0.022646886	−1.315096242
H7	−0.209708367	0.642243791	−1.904691083
H8	−1.794534121	−0.381921363	−1.798819882
H9	1.919618930	−0.284693119	−0.259088856
H10	1.401938762	−1.319229793	1.141078132
C11	−0.170995627	−1.006713879	−0.386734349
H12	−0.707034503	−1.920621467	−0.060245854
O13	0.807312297	0.000004415	0.672518733
H14	−0.954381980	0.234321308	−0.000047265
	Final geometry (E_{tot} − 265.475828)		
	X	Y	Z
C1	−0.972282536	0.318155121	0.726598152
C2	0.076764199	0.605238910	1.844522142
H3	−0.125561097	−1.313591404	−2.289641409
C4	1.123708254	−0.739911238	0.209617186
H5	−1.920053690	0.023584656	1.167485184
C6	−0.603508269	−0.535939317	−1.700502623
H7	−0.198299854	0.424087085	−2.006375641
H8	−1.666343528	−0.545678756	−1.923490096
H9	1.738978736	−0.204116972	−0.519995032
H10	1.553401797	−1.733448865	0.360067741
C11	−0.371747013	−0.772488627	−0.195793564
H12	−0.787692214	−1.741252407	0.075089354
O13	1.185774247	−0.018761265	1.476027138
H14	−1.136846936	1.251698481	0.190995350

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